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14. ABSTRACT
Nanocrystalline powders of LaB6 with an average crystallite size of 20 nm, as determined from x-ray diffraction analysis, have been obtained using a combustion synthesis technique that makes use of lanthanum nitrate, boron, and carbohydrazide as precursors. The optimum fuel-to-oxidizer ratio was found to be 0.25, which is quite low compared to typical combustion synthesis experiments. The powders are phase-pure except for about a 3 mol% contamination of LaBO3.

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Report Title

Synthesis of Nanostructured LaB6 Powders

ABSTRACT

Nanocrystalline powders of LaB6 with an average crystallite size of 20 nm, as determined from x-ray diffraction analysis, have been obtained using a combustion synthesis technique that makes use of lanthanum nitrate, boron, and carbohydrazide as precursors. The optimum fuel-to-oxidizer ratio was found to be 0.25, which is quite low compared to typical combustion synthesis experiments. The powders are phase-pure except for about a 3 mol% contamination of LaBO3.

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Graduate Students

NAME	PERCENT_SUPPORTED
Amrita Mishra	0.61
Raghunath Kanakala	0.16
Abhiram Madadi	0.11
Kaustav Sinha	0.11
FTE Equivalent:	**0.99**
Total Number:	**4**

Names of Post Doctorates

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Names of Faculty Supported

NAME	PERCENT_SUPPORTED	National Academy Member
Olivia A. Graeve	1.00	No
FTE Equivalent:	**1.00**	
Total Number:	**1**	

Names of Under Graduate students supported

NAME	PERCENT_SUPPORTED
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Brandon Williams	0.34
Adriana Velasquez	0.02
FTE Equivalent:	**1.00**
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Synthesis of Nanostructured LaB_6 Powders

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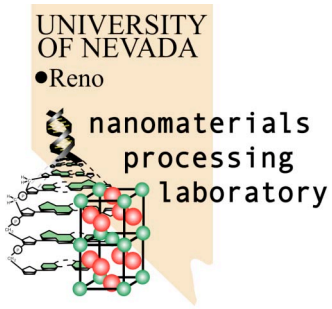
FINAL REPORT



1. INTRODUCTION

The goal of this project was to demonstrate the feasibility of preparing LaB_6 powders with an average particle size of around 50 nm via a combustion process.

Combustion synthesis [1, 2, 3, 4] has been under development in the last twenty years, and offers many advantages for the formation of ultra-fine powders. It is a wet chemical precipitation process in which an exothermic reaction between precursor components is utilized. The exothermic reaction occurs between metal nitrates and a carbonaceous fuel in a rapid and self-sustaining manner. The type of fuel and the fuel-to-nitrate ratio are the most important controlling parameters for determining the reaction temperature reached during combustion [5, 6]. In a typical combustion reaction, the precursor mixture, which is diluted in a small amount of solvent and placed in a low-temperature muffle furnace, dehydrates and ruptures into a flame in less than five minutes. As an example, the reaction shown below for Y_2O_3

$$xY\left(NO_3\right)_3 + uH_2O + Fuel \longrightarrow aY_2O_3 + bCO_2\left(g\right) + cH_2O\left(g\right) + dN_2\left(g\right)$$

is such that the products contain the desired voluminous, foamy material and gases that escape during the reaction. The gaseous products carry heat away from the system, hindering particle growth, and allowing the synthesis of powders with crystallites of nanometer dimensions, as has been shown in our recent publication [7]. The gases increase the surface area of the powders by creating micro- and nano-porous regions within the reaction zone. Computer modeling studies have shown that there are over one hundred possible product species that can be formed during the reaction [8]. However, most of the products exist in such small amounts that they can be ignored. The material in this study was synthesized using carbohydrazide (CH_6N_4O) as a fuel, since it has two desirable features: (1) it produces a very high reaction temperature, and (2) it complexes with the metal cations thereby increasing their solubility and preventing selective precipitation from occurring as the water is evaporated during the reaction. The carbohydrazide molecule has two amine groups, both of which are available to participate in the complexation of metal ions [9].

2. TECHNICAL OBJECTIVES

The specific objectives of this project were:

(1) To synthesize nanostructured powders of lanthanum hexaboride using a combustion synthesis process, and
(2) to characterize the process of synthesis over a range of experimental conditions in order to optimize the process.

3. EXPERIMENTAL RESULTS

Figure 1 illustrates the steps that were followed for the synthesis of the powders. The precursor materials, listed in **Table 1**, were mixed according to the following equation:

$$La(NO_3)_3 + 6 \cdot B + a \cdot (H_2NNH)_2 C = O \xrightarrow{\text{ethanol}} LaB_6 + x \cdot NO_2 + y \cdot H_2O + z \cdot CO_2 + \text{other gases}$$

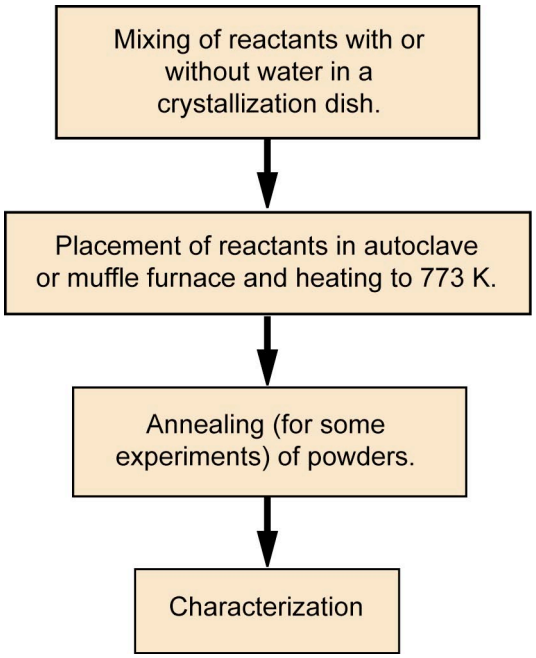


Figure 1. Process flow chart for the synthesis and characterization of the LaB_6 powders.

In regards to the viability of the process during synthesis, we have determined the optimum processing conditions for obtaining the desired powders. The parameters that were studied include:

The fuel-to-nitrate ratio is the most important parameter for the determination of the particle size and purity of the final powders, since the amount of fuel in the system determines the temperature of combustion. The mixtures that were attempted are listed in **Table 2**.

Table 1. Precursors for the synthesis of LaB_6 powders.

Precursor	Properties
$La(NO_3)_3$ Lanthanum (III) nitrate hydrate Supplier: Sigma Aldrich Catalog No: 238554	Purity: 99.9% Physical State at Room Temperature: Crystalline.
B Boron Supplier: Sigma Aldrich Catalog No: 2311512	Physical State at Room Temperature: Amorphous powder.
$(H_2NNH)_2C=0$ Carbohydrazide Supplier: Sigma Aldrich Catalog No: C11006	Purity: 98% Physical State at Room Temperature: Solid.

Table 2. Listing of all combustion experiments attempted for the project.

Fuel-to-oxidizer ratio, ϕ	Reactant amounts	Experimental conditions	Results
Experiment 1: $\phi = 4$	$m_{La(NO_3)_3 \cdot 6H_2O} = 10.6249$ g $m_B = 1.5916$ g $m_{carbohydrazide} = 8.8418$ g	Experiment in muffle furnace at 500°C using water as a solvent.	The combustion experiment resulted in a mixture of La_2O_3 and $LaBO_3$. Clearly the fuel-to-oxidizer ratio is too high and results and full oxidation of the reactants.
Experiment 2: $\phi = 0.75$	$m_{La(NO_3)_3 \cdot 6H_2O} = 10.6249$ g $m_B = 1.5916$ g $m_{carbohydrazide} = 1.6578$ g	Experiment in muffle furnace at 500°C using water as a solvent.	The x-ray diffraction analysis shows the formation of the LaB_6 phase. However, there are significant amounts of $LaBO_3$ phase. The color of the powder is brownish/purple, a sure sign for the presence of LaB_6, which is purple, and $LaBO_3$, which is brown.
Experiment 3: $\phi = 0.5$	$m_{La(NO_3)_3 \cdot 6H_2O} = 10.6249$ g $m_B = 1.5916$ g $m_{carbohydrazide} = 1.1052$ g	Experiment in muffle furnace at 500°C using water as a solvent.	The x-ray diffraction analysis shows the formation of the LaB_6 phase, with smaller amounts of the $LaBO_3$ phase.

Experiment 4: $\phi = 0.25$	$m_{La(NO_3)_3 \cdot 6H_2O} = 10.6249$ g $m_B = 1.5916$ g $m_{carbohydrazide} = 0.5526$ g	Experiment in muffle furnace at 500°C using water as a solvent.	The x-ray diffraction analysis shows the formation of the LaB_6 phase, with even smaller amounts of the $LaBO_3$ phase compared to the experiment at the $\phi = 0.5$.
Experiment 5: $\phi = 0.75$	$m_{La(NO_3)_3 \cdot 6H_2O} = 10.6249$ g $m_B = 1.5916$ g $m_{carbohydrazide} = 1.6578$ g	Experiment in muffle furnace starting at room temperature and heating to the combustion temperature of 320°C without any water. Elimination of water was attempted with the intent of reducing sources of oxygen further.	Same as experiment 2, but with smaller amounts of $LaBO_3$.
Experiment 6: $\phi = 0.5$	$m_{La(NO_3)_3 \cdot 6H_2O} = 10.6249$ g $m_B = 1.5916$ g $m_{carbohydrazide} = 1.1052$ g	Experiment in muffle furnace starting at room temperature and heating to the combustion temperature of 320°C without any water.	**Same as experiment 3, but with minimal amounts of $LaBO_3$ (about 3 mol%).**
Experiment 7: $\phi = 0.25$	$m_{La(NO_3)_3 \cdot 6H_2O} = 10.6249$ g $m_B = 1.5916$ g $m_{carbohydrazide} = 0.5526$ g	Experiment in muffle furnace starting at room temperature and heating to the combustion temperature of 320°C without any water.	**Same as experiment 3, but with minimal amounts of $LaBO_3$ (about 3 mol%).**
Experiment 8: $\phi = 0.25$	$m_{La(NO_3)_3 \cdot 6H_2O} = 10.6249$ g $m_B = 1.5916$ g $m_{carbohydrazide} = 0.5526$ g	Experiment in the protected argon atmosphere of an autoclave starting at room temperature and heating to the combustion temperature of 360°C without any water.	The x-ray diffraction analysis shows the formation of the $LaBO_3$ phase, with minimal amounts of LaB_6. We have concluded that there are still significant amounts of oxygen present during this reaction and that the $LaBO_3$ stable phase forms due to the extended higher temperatures the sample experiences during the cooling of the autoclave. The oxygen is a result of the combustion of the carbohydrazide.

As described for experiments 6 and 7, the exact phase of LaB_6 is achieved, but the $LaBO_3$ phase persists in amounts of 3 mol%. The best experiments were done in a muffle furnace with only small amount of fuel, which is unusual for combustion synthesis reactions that normally require larger amounts of fuel. The formation of the LaB_6 phase requires careful control of the temperature of reaction and immediate quenching so as not to promote the formation of the more stable $LaBO_3$ phase. The extended cooling times in the autoclave does not allow quenching of the experiment. Hence, the powders obtained for this case are mostly $LaBO_3$. The source of oxygen is the carbohydrazide. Elimination of the residual $LaBO_3$ might be possible by switching to a fuel that does not contain oxygen, such as hydrazine.

The powders from experiments 6 and 7 are the best results we have obtained. **Figure 2** shows the XRD results for these experiments.

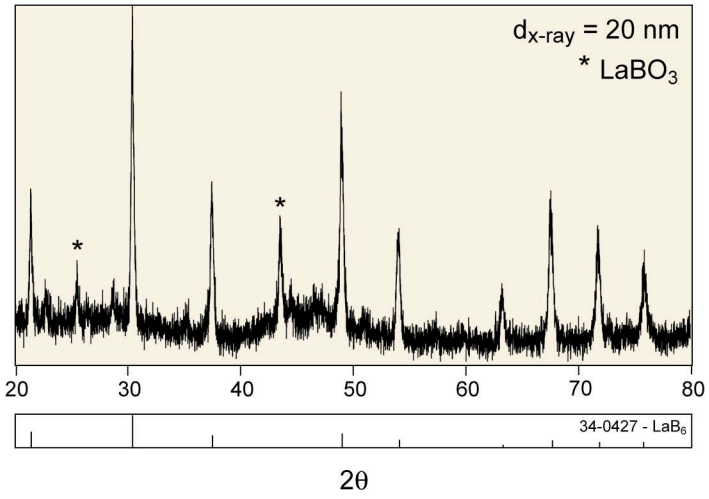


Figure 2. X-ray diffraction analysis of powders obtained using a fuel-to-oxidizer ratio of 0.25 in a muffle furnace without any solvent use for the reactants.

We have attempted to characterize the powders using scanning and transmission electron microscopy, but the powders are such strong electron emitters that it has proved impossible to focus the electron beam from the microscope column. The electrons from the sample act as strong scatterers for the electron beam, which results in images that are completely out of focus.

4. CONCLUSIONS

Nanocrystalline powders of LaB_6 with an average crystallite size of 20 nm, as determined from x-ray diffraction analysis, have been obtained using a combustion synthesis technique that makes use of lanthanum nitrate, boron, and carbohydrazide as precursors. The optimum fuel-to-oxidizer ratio was found to be 0.25, which is quite low compared to typical combustion synthesis experiments. The powders are phase-pure except for about a 3 mol% contamination of $LaBO_3$.

5. PROPOSED FUTURE WORK

1. Synthesis of the powders using hydrazine as a fuel. This fuel does not contain oxygen in its chemical formula.

2. Synthesis of the powders in a muffle furnace that allows rapid quenching of the experiment, but in an argon atmosphere. Currently our muffle furnace does not have that capability. The use of an autoclave is not advisable due to the long cooling times required for the experiment, which results in conversion of the LaB_6 into $LaBO_3$ and grain growth.

3. Development of an appropriate technique to image the powders using electron microscopy.

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